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Pentafluoropyridine as a fluorinating reagent for preparing a hydrocarbon soluble β -diketiminatolead(II) monofluoride^{†‡}

Anukul Jana, Sankaranarayana Pillai Sarish, Herbert W. Roesky,* Dirk Leusser, Ina Objartel and Dietmar Stalke*

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A well-designed method for the preparation of a β -diketiminato lead(II) monofluoride has been developed using LPbNMe₂ (L = [CH{C(Me)(2,6-*i*Pr₂C₆H₃N)}₂]) and pentafluoropyridine (C₅F₅N). The resulting LPbF was used for the synthesis of amidinatosilicon(II) monofluoride. Moreover the activation of a ketone was observed when the LPbF was treated with PhCOCF₃.

Organometallic fluorides of group 14 elements are important due to their application in synthetic methodology as well in the laboratory as in industry.¹ In the literature, the known group 14 fluoro compounds are preferentially in the +4 oxidation state.² Only few examples of organogermanium(II) and tin(II) monofluorides are known.^{3,4} In contrast, the chemistry of Pb(II) tends to be dominated by compounds with inorganic ligands. Organometallic compounds with two valent lead are relatively rare and their chemistry is poorly explored.^{5,6} Recently, we reported on a variety of lead complexes which can be used as precursors for new lead derivatives.⁷ However a fluoride derivate of lead like its lighter congener is still elusive. The difficulties with lead-based chemistry are its tendency to form insoluble precipitates besides its susceptibility to undergo redox chemistry to form metallic lead. We anticipated that the introduction of sufficiently large substituents is necessary for kinetic stabilization of such reactive species. Such a complex even as a monomer can be obtained by exploiting the unique property of the β -diketiminato ligand L (L = [CH{C(Me)(2,6-*i*Pr₂C₆H₃N)}₂]) that coordinates tightly to the lead atom, and is also capable of providing enough steric bulk to prevent the formation of oligomers. Moreover, the Pb–F bond strength is the weakest within the element(II) fluorides of group 14, due to the large Pb²⁺ radius. However at the same time relatively little is known about silicon(II) monofluorides

compared with other silicon halides, probably due to the lack of convenient synthetic routes to the fluoro compounds.⁸ This encouraged us to synthesize lead (II) and silicon (II) monofluoride. Herein we report on the synthesis of hydrocarbon soluble β -diketiminatolead(II) and amidinatosilicon(II) monofluorides and the reactivity of the former with 2,2,2-trifluoro acetophenone.

For the preparation of silicon(II) and lead(II) monofluorides initially we followed the routes which are already applied for the synthesis of germanium(II) and tin(II) monofluorides.^{3b,4b} However we were not able to obtain the expected product following this protocol. Recently, we reported on the synthesis of lead(II) amide,^{7c} e.g. LPbNMe₂ (**1**) and its reaction with ketones, where the dimethylamino group acts as a nucleophile.^{7c} Moreover, we demonstrated that the para fluorine atom of the pentafluoropyridine is easily activated by silylenes.⁹

Consequently, we treated LPbNMe₂ (**1**) in a 1 : 1 ratio with pentafluoropyridine (C₅F₅N) in diethyl ether or THF at room temperature (Scheme 1). After 12 hours it resulted in the formation of the β -diketiminatolead(II) monofluoride, LPbF (**2**) together with 4-dimethylaminotetrafluoropyridine (4-NMe₂C₅F₄N) (**3**). The ¹H NMR spectrum of the crude reaction mixture indicates the complete disappearance of the resonances for NMe₂ (δ 3.80 ppm) of **1**, and the formation of a new signal at δ 2.60 ppm for **3**. This reaction is comparable with the synthesis of 4-dimethylaminotetrafluoro-pyridine (**3**) from dimethyl amine or trimethylsilyl-dimethylamine (Me₃SiNMe₂) and C₅F₅N.¹⁰ The energy required to cleave the C–F bond is compensated by the formation of a C–N bond.

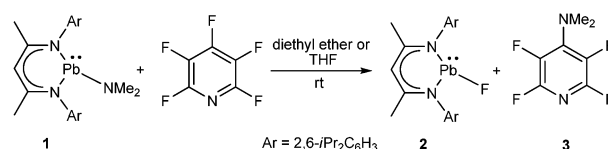
Compound **2** is a yellow solid soluble in benzene, THF, and toluene. It shows no decomposition on exposure to dry air. **2** was characterized by ¹H, ¹³C, ¹⁹F, and ²⁰⁷Pb NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. We recorded the low temperature (–80 °C) ¹⁹F and ²⁰⁷Pb NMR spectra. The ¹⁹F NMR spectrum of **2** exhibits a resonance at δ –102.7 ppm, which is accompanied

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany.

E-mail: hroesky@gwdg.de, dstalke@chemie.uni-goettingen.de; Fax: +49 551-39-3373

[†] Electronic supplementary information (ESI) available: Synthetic and spectral details. CCDC 808034 (**2**) and 808035 (**6**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11310k

[‡] Dedicated to Professor Reinhart Ahlrichs on the occasion of his 70th birthday.



Scheme 1 Synthesis of β -diketiminatolead (II) monofluoride **2**.

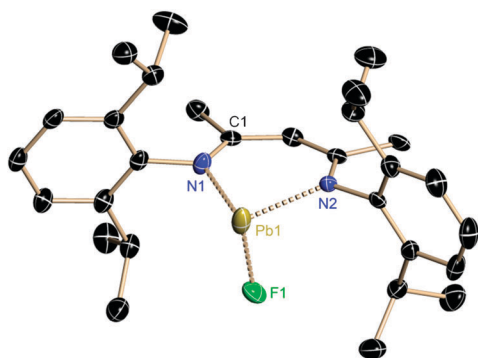
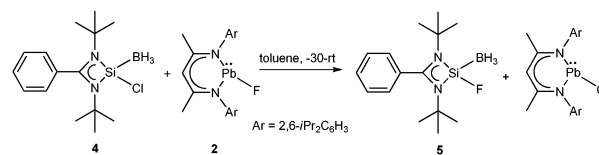


Fig. 1 Solid state structure of **2**. The anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms and the second disordered part of the molecule are omitted for clarity. The whole molecule is disordered (ratio 0.56 : 0.44). Selected averaged bond lengths (Å) and angles (°): Pb1–N1 2.317(36), Pb1–N2 2.296(34), Pb1–F1 2.088(17); N1–Pb1–N2 82(3), N1–Pb1–F1 90(4), N2–Pb1–F1 91(3).

by two ^{207}Pb satellites ($\delta -106.4$ and -99.0 ppm). The ^{207}Pb NMR spectrum shows a doublet at $\delta 787.4$ ppm, with a coupling constant of $J(^{19}\text{F}-^{207}\text{Pb}) = 2792$ Hz, which is upfield shifted when compared with that of **1** ($\delta 1674$ ppm).^{7c} The satellite resonances and coupling constants of the ^{19}F and ^{207}Pb NMR spectra are not observed, when the measurements are carried out at room temperature. This suggests that the Pb–F bond is kinetically labile on the NMR time scale at room temperature. Dissolving **2** in hot *n*-hexane and keeping it for two days at -32 °C resulted in yellow single crystals suitable for X-ray structural analysis.† **2** crystallizes in the monoclinic space group $P2_1/n$, with one molecule in the asymmetric unit (Fig. 1).§ Compound **2** exists as a monomer in the solid state with a terminal bound fluorine atom, which has the potential to be used as a fluorinating agent. The coordination polyhedron around the lead atom comprises two nitrogen atoms from the supporting ligand, one fluorine atom, and one lone pair featuring a distorted tetrahedral geometry. The Pb–F bond length is 2.088(17) Å, obviously longer when compared with those of Ge–F (1.805(17) Å) in LGeF^{3b} and Sn–F (1.988(2) Å) in LSnF^{4b} . The average Pb–N bond lengths are 2.317(36) and 2.296(34) Å, and slightly longer than the Pb–N bond lengths in **1** (2.155(10) Å).

After the isolation of lead(II) monofluoride, we focused on the synthesis of silicon(II) monofluoride. The stable LPbF contains a terminal fluorine atom, which can serve as a nucleophilic reagent. However, the reaction of silicon(II) chloride L^1SiCl [$\text{L}^1 = \text{PhC}(\text{N}t\text{Bu})_2$]¹¹ with Me_3SnF , LGeF , LSnF , and LPbF , respectively, as a fluorinating reagent mostly resulted in the formation of L^1SiF_3 and some unidentified products. Finally we used $\text{L}^1\text{SiCl}(\text{BH}_3)$ (**4**)¹³ instead of L^1SiCl , and treated this compound with LPbF .

The 1 : 1 reaction of $\text{L}^1\text{SiCl}(\text{BH}_3)$ with LPbF in toluene at -30 °C leads to the formation of $\text{L}^1\text{SiF}(\text{BH}_3)$ (**5**) and LPbCl (Scheme 2). Compound **5** is a white solid soluble in benzene, toluene, and THF and shows no decomposition on exposure to dry air. It was characterized by ^1H , ^{11}B , ^{13}C , ^{19}F , and ^{29}Si NMR spectroscopy, EI mass spectrometry, and elemental analysis. The resonance corresponding to the *tert*-butyl



Scheme 2 Synthesis of an organosilicon(II) monofluoride **5**.

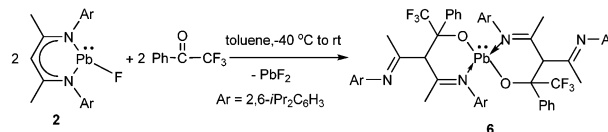
protons appears as a singlet ($\delta 1.0$ ppm) in the ^1H NMR spectrum. The ^{19}F NMR spectrum of the reaction mixture exhibits the consumption of lead(II) monofluoride and indicates the formation of a new ^{19}F resonance at $\delta -121.59$ ppm, which is accompanied by ^{29}Si satellite signals ($J = 438.17$ Hz). The ^{29}Si NMR spectrum shows a doublet of quartets ($\delta 23.63$ ppm and $J(^{29}\text{Si}-^{11}\text{B}) = 66.78$ Hz) indicative for one silicon–boron and silicon–fluorine bond. The ^{11}B NMR spectrum is also consistent with the presence of one BH_3 group. No molecular ion peak was found in the EI mass spectrum of **5**, but the most intense peak corresponds to $[\text{M}^+ - \text{BH}_3]$. Therefore we conclude the preparation of silicon(II) monofluoride, $\text{L}^1\text{SiF}(\text{BH}_3)$ (**5**), was successful.

Here it is worth mentioning that Jutzi *et al.* reported the formation of unstable Cp^*SiF (where Cp^* indicates 1,2,3,4,5-pentamethylcyclopentadienyl), which is highly reactive and dimerizes to the unstable disilene $\text{Cp}^*(\text{F})\text{Si}=\text{Si}(\text{F})\text{Cp}^*$, which further reacts to the isolable cyclotetrasilane by a [2 + 2] cycloaddition.¹⁴

After the successful reaction of **2** with **4**, we turned our attention to the activated ketone, 2,2,2-trifluoro-acetophenone. The reaction of **2** with PhCOCF_3 leads to the formation of homoleptic Pb(II) compound, $\text{L}'_2\text{Pb}$ [$\text{L}' = \text{CH}(\text{CPhCF}_3\text{O})-\text{C}(\text{Me})(=2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2$] (**6**) in good yield (Scheme 3).

This reaction is quite different when compared with those of LGeH or LSnH and PhCOCF_3 .¹⁵ In the latter case the nucleophilic addition reactions occurred under formation of germanium(II) or tin(II) alkoxide, respectively.

Single crystals suitable for X-ray structural analysis† were obtained when a concentrated solution of **6** in a mixture of THF and *n*-pentane was stored at -5 °C. **6** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit.§ The structure of **6** (Fig. 2) reveals the homoleptic nature of the complex and contains two six-membered OC_3NPb rings, that are connected by the common lead atom. Thus, the Pb atom is four-coordinate and adopts a distorted trigonal bipyramidal geometry with two nitrogen atoms of the β -diketiminato ligand occupying the axial positions, two oxygen atoms, and the lone pair residing in the equatorial positions. As expected, the average Pb–N (2.620_{av} Å) bond length is longer than those of the corresponding bonds in **2** (2.307_{av} Å). The average Pb–O bond distance (2.169_{av} Å) is longer than that in $\text{LPbO}i\text{Pr}$ (2.135(3) Å) and $\text{LPbO}t\text{Bu}$ (2.126(3) Å).¹⁶



Scheme 3 Synthesis of a homoleptic lead(II) complex **6**.

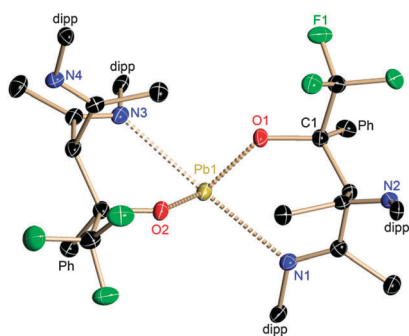


Fig. 2 Solid state structure of **6**. The anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms, the phenyl groups (Ph), and the 2,6-diisopropylphenyl moieties (dipp) are omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1–N1 2.6075(16), Pb1–N3 2.6319(16), Pb1–O1 2.1679(13), Pb1–O2 2.1707(14); N1–Pb1–O1 77.37(5), N3–Pb1–O1 93.24(5), N3–Pb1–N1 166.23(5), O1–Pb1–O2 85.09(5).

6 has been also characterized by spectroscopic and analytic measurements in addition to the X-ray structural analysis. The ^1H NMR spectrum of **6** agrees with the solid state structure. Two singlet resonances were observed for the methyl (δ 2.96 and δ 1.86 ppm) and the *CH* protons also appear as another singlet at δ 5.19 ppm. In the ^{19}F NMR spectrum of **6** the *C–F* resonance appears as a sharp singlet at δ -76.2 ppm. This shows an upfield shift compared to that of the ketone, PhCOCF_3 (δ -71.6). The ^{207}Pb NMR spectrum of **6** exhibits a singlet which is shifted downfield (δ 853.9 ppm), when compared with **2** (δ 787.4 ppm). Compound **6** is found to be sensitive towards moisture and air and it is soluble in benzene, THF, toluene, and diethyl ether.

In conclusion, after the successful syntheses of amidinato-silicon(II) and β -diketiminatolead(II) monofluorides, the series of fluorides with the heavier low valent group 14 elements has been completed, although the corresponding stable fluoride of low valent carbon remains still elusive. The reaction of lead(II) monofluoride with PhCOCF_3 results in a homoleptic lead compound in which the ketone is incorporated. Currently we are investigating the reactivity of this lead(II) monofluoride as fluorinating reagent.

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Notes and references

§ Crystal data for **2**: $\text{C}_{29}\text{H}_{41}\text{FN}_2\text{Pb}$, $M_r = 643.84$, $0.05 \times 0.1 \times 0.1$ mm, $a = 11.7697(16)$, $b = 20.465(3)$, $c = 11.7727(16)$ Å, $\beta = 95.906(2)$, $V = 2820.6(7)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.516$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 6.066$ mm⁻¹, $2\theta_{\text{max}} = 61^\circ$, 90262 reflections measured, 8667 independent ($R_{\text{int}} = 0.039$), $R_1 = 0.021$ ($I > 2\sigma(I)$), $wR_2 = 0.0503$ (all data), res. density peaks: 3.12 to -1.41 e Å⁻³; crystal data for **6**: $\text{C}_{74}\text{H}_{92}\text{F}_6\text{N}_4\text{O}_2\text{Pb}$, $M_r = 1390.71$, $0.15 \times 0.15 \times 0.1$ mm, $a = 15.7060(15)$, $b = 18.9000(18)$, $c = 26.336(3)$ Å, $\beta = 107.0930(10)$, $V = 7472.3(12)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.236$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 2.316$ mm⁻¹, $2\theta_{\text{max}} = 52^\circ$, 1666483 reflections measured, 14728 independent ($R_{\text{int}} = 0.0387$), $R_1 = 0.0208$ ($I > 2\sigma(I)$), $wR_2 = 0.0543$ (all data), res. density peaks: 0.717 to -1.197 e Å⁻³.

CCDC 808034, 808035 contain the supplementary crystallographic data for **2** and **6**.

- 1 E. F. Murphy, R. Murugavel and H. W. Roesky, *Chem. Rev.*, 1997, **97**, 3425–3468.
- 2 See examples of fluorides in +4 oxidation state of group 14: (a) G. V. Odabashyan, V. A. Ponomarenko and A. D. Petrov, *Russ. Chem. Rev.*, 1961, **30**, 407–426; (b) A. P. Kostikov, L. Iovkova, J. Chin, E. Schirmacher, B. Wängler, C. Wängler, K. Jurkschat, G. Cosa and R. Schirmacher, *J. Fluorine Chem.*, 2011, **132**, 27–34; (c) K. Junold, C. Burschka, R. Bertermann and R. Tacke, *Dalton Trans.*, 2010, **39**, 9401–9413; (d) M. Mehring, I. Vrasidas, D. Horn, M. Schürmann and K. Jurkschat, *Organometallics*, 2001, **20**, 4647–4653; (e) W.-P. Leung, W.-H. Kwok, Z.-Y. Zhou and T. C. W. Mak, *Organometallics*, 2003, **22**, 1751–1755; (f) R. A. Varga, K. Jurkschat and C. Silvestru, *Eur. J. Inorg. Chem.*, 2008, 708–716; (g) D. J. Brauer, H. Bürger and R. Eujen, *Angew. Chem.*, 1980, **92**, 859–860 (*Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 836–837); (h) E. Lukevics, S. Belyakov, P. Arsenyan and J. Popelis, *J. Organomet. Chem.*, 1997, **549**, 163–165.
- 3 (a) P. Rivière, J. Satgé, A. Castel and H. Normant, *C. R. Acad. Sci. Paris*, 1976, **282**, 971–974; (b) Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2001, **20**, 4806–4811.
- 4 (a) R. W. Chorley, D. Ellis, P. B. Hitchcock and M. F. Lappert, *Bull. Soc. Chim. Fr.*, 1992, **129**, 599–604; (b) A. Jana, H. W. Roesky, C. Schulzke, A. Döring, T. Beck, A. Pal and R. Herbst-Irmer, *Inorg. Chem.*, 2009, **48**, 193–197; (c) A. Jana, H. W. Roesky, C. Schulzke and P. P. Samuel, *Organometallics*, 2010, **29**, 4837–4841.
- 5 Review: (a) M. Driess and H. Grützmacher, *Angew. Chem.*, 1996, **108**, 900–929 (*Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 828–856); (b) P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268–2274; (c) S. Wingerter, H. Gornitzka, R. Bertermann, S. K. Pandey, J. Rocha and D. Stalke, *Organometallics*, 2000, **19**, 3890–3894.
- 6 (a) M. Kaupp and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1993, **115**, 1061–1073; (b) K. Jurkschat, K. Peveling and M. Schürmann, *Eur. J. Inorg. Chem.*, 2003, 3563–3571 and references therein.
- 7 (a) A. Murso, M. Straka, M. Kaupp, R. Bertermann and D. Stalke, *Organometallics*, 2005, **24**, 3576–3578; (b) A. Jana, S. P. Sarish, H. W. Roesky, C. Schulzke, A. Döring and M. John, *Organometallics*, 2009, **28**, 2563–2567; (c) A. Jana, H. W. Roesky, C. Schulzke, P. P. Samuel and A. Döring, *Inorg. Chem.*, 2010, **49**, 5554–5559.
- 8 (a) P. L. Timms, *Inorg. Chem.*, 1968, **7**, 387–389; (b) P. L. Timms, R. A. Kent, T. C. Ehlert and J. L. Margrave, *J. Am. Chem. Soc.*, 1965, **87**, 2824–2828.
- 9 A. Jana, P. P. Samuel, G. Tavčar, H. W. Roesky and C. Schulzke, *J. Am. Chem. Soc.*, 2010, **132**, 10164–10170.
- 10 (a) R. E. Banks, J. E. Burgess, M. Cheng and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 575–581; (b) L. I. Goryunov, V. D. Shteingarts, J. Grobe, B. Krebs and M. U. Triller, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1770–1779.
- 11 (a) C.-W. So, H. W. Roesky, J. Magull and R. B. Oswald, *Angew. Chem.*, 2006, **118**, 4052–4054 (*Angew. Chem., Int. Ed.*, 2006, **45**, 3948–3950); (b) S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, *J. Am. Chem. Soc.*, 2010, **132**, 1123–1126.
- 12 R. S. Ghadwal, K. Pröpper, B. Dittrich, P. G. Jones and H. W. Roesky, *Inorg. Chem.*, 2011, **50**, 358–364.
- 13 A. Jana, D. Leusser, I. Objartel, H. W. Roesky and D. Stalke, *Dalton Trans.*, 2011, DOI: 10.1039/c0dt01675f.
- 14 P. Jutzli, U. Holtmann, H. Bögge and A. Müller, *J. Chem. Soc., Chem. Commun.*, 1988, 305–306.
- 15 (a) A. Jana, H. W. Roesky and C. Schulzke, *Dalton Trans.*, 2010, **39**, 132–138; (b) A. Jana, H. W. Roesky, C. Schulzke and A. Döring, *Angew. Chem.*, 2009, **121**, 1126–1129 (*Angew. Chem., Int. Ed.*, 2009, **48**, 1106–1109).
- 16 E. C. Y. Tam, N. C. Johnstone, L. Ferro, P. B. Hitchcock and J. R. Fulton, *Inorg. Chem.*, 2010, **49**, 5554–5559.